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Kinetic Study in the Extraction of Essential Oil from Clove (*Syzgium aromaticum*) Stem using Microwave Hydrodistillation

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Abstract

On understanding the potential significance of the microwave-assisted extraction, studying the kinetics mechanisms and modeling of the extraction method is necessary. The aim of this study was to evaluate the suitable kinetic models for microwave hydrodistillation (MHD) of the essential oil from clove (*Syzgium aromaticum*) stem. MHD was performed of 100 g dried clove stem in 200 mL aquadest, heated at various power settings of 300, 450, 600 and 800 W. The extraction conducted for a total of 120 min with 10 min intervals. The experimental data (extract yields versus time) were fitted to four-two parameter empirical kinetic models. The total extract yields from clove stem oil exhibited a close fit to the hyperbolic model and Weibull's exponential. The result also suggested that the increase in microwave irradiation power significantly affected some of the parameter of MHD kinetic models.

Keywords: *Syzgium aromaticum; Clove stem; Microwave hydrodistillation; Extraction kinetics; Empirical models*

1. Introduction

The phytochemical compounds contained in plants are sources of chemicals that can be used in various industrial interests, such as food & beverage, pharmaceutical, cosmetics, pesticides and other chemical industries. Essential oil is one of the important phytochemicals which is a mixture of various bioactive compounds. Essential oil or etheric oil is a type of volatile oil that comes from plants and has a distinctive aroma. Essential oils and their derivatives are types of non-oil and gas export commodities with broad benefits so that they have a huge potential for sale value. Cloves (*Syzygium aromaticum*) are potential aromatic plants that are widely cultivated in tropical and sub-tropical regions. Indonesia is one of the largest global clove producer, with a total production capacity per year reaching 140 thousand tons in 2016 [1], and has been used as a food flavoring, components for tobacco, oleoresin and essential oils. Clove oil is a type of essential oil which is Indonesia's main export commodity, with a total production of 63% of the total global essential oil commodity production [2]. The main benefit obtained from essential oils rich in cloves is the content of eugenol and eugenyl acetate, that are two of essential chemicals required in food and cosmetics industries. Cloves contain volatile oil in significant amounts, wether in flowers (10-20%), stems (5-10%), and leaves (1-4%) [3]. Of the three parts, the clove stem is still rarely utilized so that it has the potential to be developed. Currently, the production of essential oil, specifically clove oil, in Indonesia are still using conventional methods such as steam distillation. Processing of essential oils with conventional methods has several disadvantages such as large energy requirements, long extraction times, large solvent requirements, loss of several important volatile compounds, low extraction efficiency, and toxic solvent residues. Various new methods for extracting essential oils have been developed taking into account the minimization of solvent as well as energy use, including supercritical fluid technology and microwave-assisted extraction (MAE). Studies on MAE show that the extraction method was successfully applied in extracting essential oils on a laboratory scale and various configuration schemes of extraction equipment have been proposed. One of the promising MAE technologies is microwave hydrodistillation (MHD) that offers the potential to be applied on an industrial scale because of its simple yet economical tool configurations and could generate high yields of products [4], [5]. MHD method is a combination of a distillation system with water used as solvent (hydrodistillation) with the assistance of microwave heating. This method provides unique features and advantages which are suitable for specific extraction processes. The non-conventional extraction methods are presumed to be the alternative approaches, even to replace conventional solvent extractions, that makes studying the kinetics mechanisms and modeling essential. Such studies could benefit prediction of the extraction behavior which is considered to be useful for further application or scaling up of the process. To the best of our knowledge, however, there are still limited studies that have been documented on kinetic models for MHD of clove stem oil. The aim of this study was to evaluate the suitable kinetic models for MHD of clove stem oil and to gain better understanding of the microwave power effects on the extraction rate and the correlation with the kinetic models' parameters.

2. Experimental

2.1. Materials

In this study, clove stems were obtained from Malang, East Java. The stems were sun-dried, and the moisture content was determined by drying at 105°C to constant weight, was about 15%. Aquadest was used for solvent during MHD experiment. All chemicals used were of analytical grade.

2.2. Microwave-assisted Hydrodistillation (MHD) of Clove Stem Oil

Extraction experiments were carried out using a modified domestic microwave oven (Electrolux EMM2308X, 800 W, 2.45 GHz) applicable for conducting hydrodistillation. The dimension of the PTFE-coated cavity of the oven were 485

x 292.5 x 370 mm. The experimental setup of MHD apparatus used in the current work is on the basis of the previous studies [6], [7]. 100 grams of clove stems were placed in a 1000 mL one-neck rounded flask containing aquadest (200 mL). Samples were then heated at various power settings of 300, 450, 600, and 800 W. The total extraction time was 120 min at 10 min intervals. The collected clove stem oils were weighed and stored in amber vials at 4°C. The extraction yield is calculated according to Equation 1.

$$\bar{q} = \frac{q}{q_0} \qquad (1)$$

Where q is the amount of oil extracted while q_0 is the amount of oil present in clove stem material in g/100g of clove stem material.

2.3 Empirical Kinetic Models

Four two-parametric kinetic models that are frequently used in extracting solutes from various sources of solid materials were evaluated: power law, hyperbolic, Weibull's exponential equation, and Elovich's equation.

2.3.1 Power Law Model

The power law model is used to express the extraction mechanism by the diffusion compounds through non-swelling devices [8], [9] Where t is time (min), B is a constant incorporating the characteristics of the carrier–active agent system, and n is the diffusional exponent which indicative of transport mechanisms. For extraction of plant materials, the values of n is < 1.

$$\bar{q} = Bt^n \qquad (2)$$

2.3.2 Hyperbolic model

The hyperbolic model which applied as Peleg's model [8]:

$$\bar{q} = \frac{C_1 t}{1 + C_2 t} \qquad (3)$$

Where t is time (min), C_1 is the extraction rate at the very beginning (min^{-1}) and C_2 is a constant that is related to maximum extraction yield (min^{-1}). The rate of the extraction process is first order at the very start and decreases to zero-order in the very late of the process.

2.3.3 Weibull's exponential equation

The Weibull's equation that describes the extraction of clove stem oil or other plant material by the following equation [10]:

$$\bar{q} = 1 - \exp\left(-\frac{t^m}{D}\right) \qquad (4)$$

Where D is the scale parameter which represents the process' time scale and m is the shape parameter of the curve. If m < 1 the shape of the curve is parabolic with a high initial slope followed by an exponential shape typical for an extraction process. If m= 1, the curve is an exponential curve, whereas if m > 1 the curve is characterized by an S-shaped with upward curvature followed by turning point.

2.3.4 Elovich's logarithmic equation

A modified form of Elovich's equation is in the form of a logarithmic equation:

$$\bar{q} = E_0 + E_1 \times \ln t \qquad (5)$$

Where E_0 and E_1 are parameters of the Elovich equation (L). The Elovich's equation, which is widely applied to chemisorptions [11], signifies that the extraction rate of a substance declines exponentially with the increasing of the extraction yield ($dy/dt = \beta \exp^{-\alpha y}$).

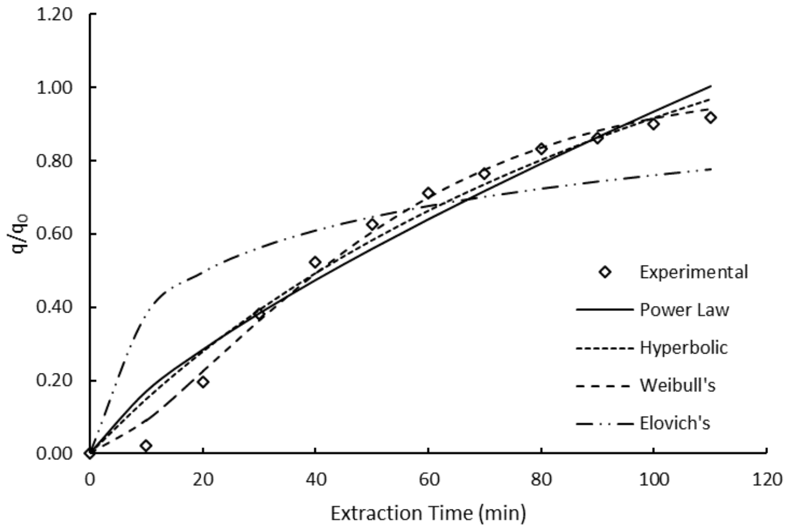
2.4 Statistical analysis

The statistical analysis that is used to evaluate the models in this study is the coefficient of determination. The coefficient determination is a statistical measure indicates how well data fit a statistical model, R^2:

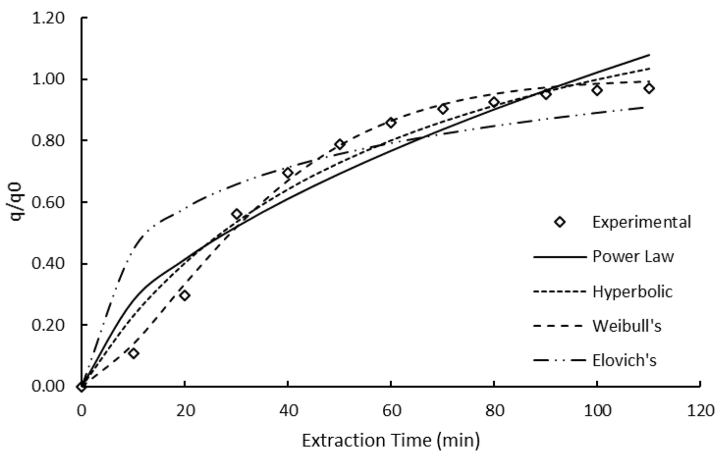
$$R^2 = \frac{\sum_{i=1}^{n}(q_{p,i}-q_{a,i})^2}{\sum_{i=1}^{n}(q_{p,i}-q_m)^2} \quad (6)$$

3. Results and discussion

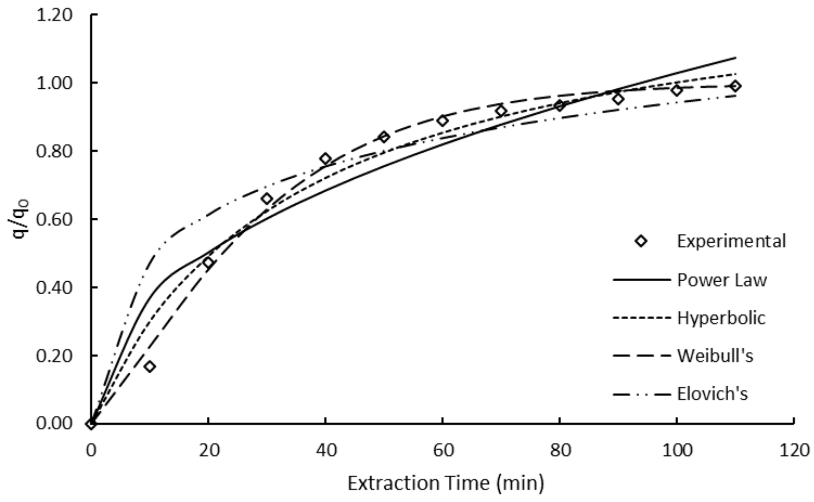
The kinetics of clove stem oil extraction using microwave as heating source were evaluated, as presented on Figure 1..



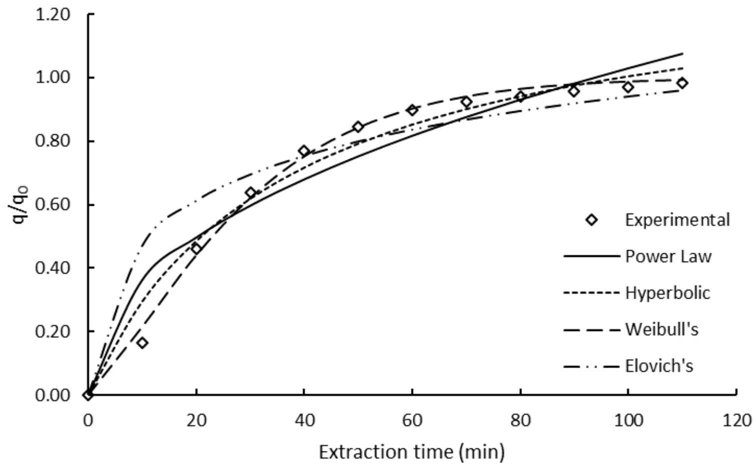
(a)



(b)



(c)



(d)

Figure 1. Comparison of experimental (symbols) and fitted (line) yields for the extraction of essential oil from clove (*S. aromaticum*) stem at different operating microwave power (a) 300 W, (b) 450 W, (c) 600 W, (d) 800 W (Operating conditions: F/S of 0.50 g/mL; total extraction time of 110 min)

The extraction yield of clove stem oil in various power settings were fitted to four-two parametric empirical kinetic models that are previously mentioned. Further analyzing the experimental kinetic curve of the microwave hydrodistillation of the clove stem shows that the curve did not exhibited the typically solvent extraction curve comprised of two stages: a fast extraction stage (washing stage) and a slow extraction stage (diffusion stage). The curves representing the change of clove stem oil yield in MHD experiment were sigmoid or S-shaped with upward curvature towards the ordinate. According to Figure 1, for most power settings, three kinetic steps can be observed; an almost linear increase during the initial step of the microwave hydrodistillation, followed by the rapid increase of the extract yield at 20-70 minutes (second step) and became slowly increased with longer extraction time until it reached constant after 90 minutes of extraction. Up to 90% of the total oil recovery extracted during the second part. The result is dissimilar with [8] which stated that the solvent extraction of extractive substances from plant materials usually provides a parabolic kinetic curve, depicting the change of yield upon time with a high initial slope followed by an exponential shape. Similar findings of a sigmoid variation of the essential oil yield with time was observed for some

plant materials extracted by water or steam distillation [12], such as rosemary [13] and *Artemisia judaica L.* [14]. Furthermore, [7] has also reported that a microwave extraction process takes place in three different periods namely an equilibrium phase, an intermediary transition phase, and diffusion phase. The diffusion rate will decrease when prolonging time due to the high concentration of solute in the third phase thus yielded insignificant amount of extractable substances. Upon evaluating the best kinetic model that represent the experimental data, the coefficient of determination (R^2) was used. The higher the value of R^2, the better will be the goodness of model fit to the experimental data. Table 1 summarizes the R^2 value and the correlation coefficient for different kinetic models. For all values of the microwave power, the hyperbolic and Weibull's models were a close fit to the experimental data with a relatively large R^2 values (0.9700-0.9963). The hyperbolic model is most applicable for an extraction that is first-order at the very beginning and declines to zero-order in the latter stage of the process, indicating that the yield reaching its maximum and/or plateau [8], [15]. Meanwhile, Weibull's exponential two-parameter model have been previously applied to the extraction of natural substances from plant materials and provided fairly R^2 results, implying good agreement between experimental and model data [16]. Among the four models, the Elovich's model attained the smallest R^2 values (0.8040-0.9193) for all power settings and can be considered unsuitable for MHD kinetics for clove stem materials. Furthermore, the effect of the microwave power on the models' coefficients as presented in Table 1 indicates that as microwave power increases, the parameters B, C_1, C_2, E_1 generally were also enhanced, except n, m, and D which decreased, as well as E_0 which did not change. In other words, most of the kinetic model parameters such as B, C_1, C_2, E_1 increased with elevated irradiation power. However, when the power level was increased up to 800W, the opposite influence of the irradiation power on the kinetic parameters was observed. The decrease in yield was also apparent upon increasing the power level to 800W. The result suggested that the poor obtained yield may be the result of overheating that led to undesired solvent extraction [17], thermal degradation of heat sensitive substances [18], and the affected stability of target compounds such as reported in [19]. Parameter of the Power Law models' constant B describes the characteristics of the carrier-active agent that could represent the behavior of water as an extraction solvent. In MHD method, water acts as the carrier of the volatile substances during the evaporation process before the condensation took place. It could be noted from Table 1 that at higher microwave intensities, the values of B are also increased indicating the enhanced ability of water to absorb the heat generated and transfer certain amount of the heat for plant matrix disruption. Thereby, releasing its extractable contents into the liquid phase. In a microwave-assisted extraction, the microwave irradiation power is interrelated with the process temperature. Consequently, greater power levels used generates temperature rise which in turn increase the penetrability and solubility of the solvent. A rise in temperature also decreases the solvent viscosity and surface tension, thus leads to better interaction with plant matrix and results in higher yields and extraction rate. Meanwhile, the transport mechanism of the process characterized by a smaller value of the diffusional exponent n ($n < 1$), decreased with increasing temperature. This result indicates the ease of solute transfer during the washing and diffusion stage [19] in the extraction process. The washing stage of clove stem oil extraction corresponds to the extraction of accessible solute fraction that mostly located on the surface of the plant matrix [13], [17]. Observed variations on other kinetic models' parameters also exhibited a prominent effect of the microwave power. The values of hyperbolic model parameters signify that the initial extraction rate and the maximum extraction yield constant, C_1 and C_2 respectively, increase upon microwave irradiation. Furthermore, a significant decrease was observed on the Weibull's scale parameter (D) which represents time scale of the process as the increase in the power magnitude. The D parameter could describe the time needed when the equilibrium is reached. Thus, the decreasing value of D could indicate that as the microwave power increased, the needed time for extraction process to reach its maximum yield is accelerated. As briefly discussed before, the principles of MHD process are different from those of conventional methods because the extraction in microwave assisted heating occurs

as the result of changes in the cell structure caused by electromagnetic waves. When the heat from the microwave moves to the water content in the plant material cells, there is an evaporation process follows by expansion, then produces high pressure on the cell walls of the oil glands. The resulting internal pressure pushes out the cell walls of the oil glands and makes the cell wall break. This event facilitates the process of releasing essential oils from plant material to surrounding solvents (water). This phenomenon can be improved if plant material is immersed in solvents such as water with higher dissipation factor. High temperatures absorbed by plant cell walls can reduce the mechanical strength of plants and increase the swelling of plant material, which increased the contact surface area between the plant matrix and the solvent. Some previous studies that have experimentally investigated the drug release from swellable materials using Weibull's equation model [20] shown that the model is favorable in describing the release kinetics from swellable materials. Similar behavior of swellable plant materials can also be expected from MHD experiment

Table 1: Parameters of Power Law, Hyperbolic, Weibull's and Elovich's model for extraction of essential oil from dried clove (*S. aromaticum*) stem using microwave hydrodistillation method

Microwave	**Power Law**			**Hyperbolic**			**Weibull's**			**Elovich's**		
Power (W)	B	n	R^2	C_1	C_2	R^2	D	m	R^2	E_0	E_1	R^2
300	0.0307	0.7420	0.9591	0.0160	0.0074	0.9780	272.7955	1.4146	0.9935	0	0.1651	0.8040
450	0.0770	0.5615	0.9339	0.0270	0.0170	0.9700	188.1903	1.4480	0.9952	0	0.1938	0.8647
600	0.1326	0.4450	0.9368	0.0387	0.0286	0.9782	65.9710	1.2303	0.9943	0	0.2050	0.9193
800	0.1275	0.4535	0.9355	0.0375	0.0274	0.9775	75.9872	1.2644	0.9963	0	0.2042	0.9146

4. Conclusion

The kinetics of clove stem oil extraction by MHD with different power settings has been evaluated using four-two parameter empirical kinetic models: power law, hyperbolic, Weibull's, and Elovich's equation. Most of the models tested were shown to be suitable to model the clove stem oil kinetics under operating conditions employed. A relatively high values of R^2 (> 0.93) demonstrates good agreement between experimental data and kinetic models applied. The Weibull's exponential equation gave the best fit to represent MHD of clove stem oil kinetics. This model (with the highest R^2 value of 0.9963) fitted to the experimental data better than the other three kinetic models. Furthermore, it was also observed that the increase of microwave irradiation power significantly affected the decrease of the Weibull's scale parameter. It can be concluded that an increase in the value of irradiation power could affects the rate of reaction which leads to a higher extraction yield in shorter extraction time.

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